



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C23C 16/08, 16/30, 16/50</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 96/18756</b> <b>(43) International Publication Date:</b> 20 June 1996 (20.06.96)
<b>(21) International Application Number:</b> PCT/DK95/00505 <b>(22) International Filing Date:</b> 15 December 1995 (15.12.95) <b>(30) Priority Data:</b> 1436/94 16 December 1994 (16.12.94) DK <b>(71) Applicant (for all designated States except US):</b> NKT RE-SEARCH CENTER A/S [DK/DK]; Sognevej 11, DK-2605 Brøndby (DK). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> GLEJBØL, Kristian [DK/DK]; Fiskerhusene 8, DK-2620 Albertslund (DK). PRYDS, Nini, Hamawi [IL/DK]; Olof Palmesgade 9, st. th., DK-2100 Copenhagen Ø (DK). <b>(74) Agent:</b> HOFMAN-BANG & BOUTARD A/S; Adelgade 15, DK-1304 Copenhagen K (DK).		<b>(81) Designated States:</b> JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> A PA-CVD PROCESS FOR DEPOSITION OF A SOLID METAL-CONTAINING FILM ONTO A SUBSTRATE CONTAINING AT LEAST 50 % of Fe or WC		
<b>(57) Abstract</b>  A new plasma assisted chemical vapour deposition (PA-CVD) process for deposition of a solid metal-containing film onto the surface of a substrate containing at least 50 % of Fe or WC (such as hard metal or steel), by which the metallic component of the metal-containing film is introduced into the system as a metal halide, is disclosed. The new process involves shifting the process gas composition between a high and a low metal halide level, whereby the adhesion of the deposited film to the substrate is improved.		

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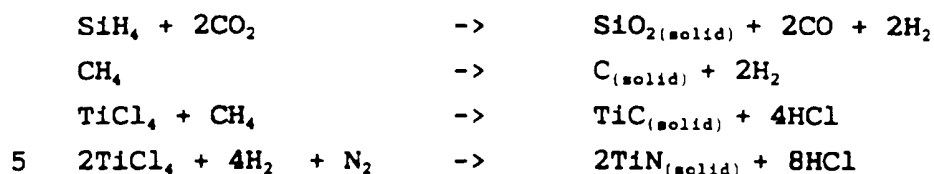
A PA-CVD process for deposition of a solid metal-containing film onto a substrate containing at least 50% of Fe or WC

5 The present invention is directed to a plasma assisted chemical vapour deposition (PA-CVD) process for deposition of a solid metal-containing film onto the surface of a substrate containing at least 50% of Fe or WC, by which the metallic component of the solid metal-containing film is introduced into the system as a metal halide.

A CVD process is commonly defined as a chemical reaction of gaseous film-forming compounds close to, or on a surface, resulting in solid deposits and volatile waste products. Most often the reaction takes place in a closed vessel in order to avoid contamination from the ambient atmosphere. To promote the reactions, activation of the gas is often necessary. The methods of activation includes heating of the gas (thermal activation) and excitation of the gas by electric fields (plasma activation). Often a combination of different excitation methods is used. When excitation of the gas by electrical fields is employed, the process is normally referred to as plasma assisted chemical vapour deposition (PA-CVD).

25 Although the reaction resulting in the solid deposit has to run at or near the surface, precursors important to this reaction are often formed in the gas phase. As an example,  $\text{TiCl}_2$  is an important precursor for the synthesis of  $\text{TiN}$  from  $\text{TiCl}_4$ ,  $\text{N}_2$  and  $\text{H}_2$ .  $\text{TiCl}_2$  is believed to be formed in the free gas according to the reduction reaction  $\text{TiCl}_4 + \text{H}_2 \rightarrow \text{TiCl}_2 + 2\text{HCl}$ . After formation the  $\text{TiCl}_2$  molecules diffuse to the surface.

Below are given a few important examples:



In the above reaction schemes, formulae on the left-hand side of the arrows represent gaseous film-forming compounds and formulae on the right-hand side of the arrows represent the resulting deposits (indicated by the subindex "solid") and volatile waste gases.

Prior art techniques for CVD deposition of metal-containing films are often vitiated by the drawback that the solid deposit and/or the interface between the substrate and the deposit is contaminated by adsorbed waste gas and/or film-forming precursors. Thus, CVD processes for the deposition of metal-containing films by which the metallic component of the deposit is introduced into the system as a metal halide often result in halogen-contaminated films.

Kazuki Kawata describes in Surface and Coatings Technology, Vol. 54/55 (1992), pp. 604-608 CVD processes for deposition of TiN, TiC and Ti(C,N) films on steel substrates and CVD equipment suitable for mass-productional operation. As an example of a gas composition suitable for TiN film coating the following is mentioned:  $\text{N}_2:\text{Ar}:\text{H}_2:\text{TiCl}_4 = 18.8:4:75:2.2$ . During a PA-CVD process this gas composition is contacted with a substrate surface at a pressure of 1.3 to  $1.3 \times 10^3$  Pa and a temperature of 573 to 873 K. However, we have found that the TiN film formed according to these process parameters often suffers from Cl-contamination and insufficient adherence of the deposited film to the substrate.

1976, pp. 257-261 a CVD process for deposition of tungsten

coatings according to the reaction  $WF_6 + 3H_2 \rightarrow W + 6HF$ . In this process deposits of uniform thickness are obtained by pulsing the  $WF_6$  and  $H_2$  gas pressure in the deposition chamber. More specifically the process consists of intermit-

5 tently injecting reactant gasses into a previously evacuated chamber. By using nominal pressures during deposition and evacuation of 15 Torr and 2 Torr, respectively, deposition and evacuation periods of 10 seconds and 5 seconds, respectively, and 5800 cycle repetitions, a W layer having a

10 thickness of 0,75 mm is deposited.

US-A-5 279 857 describes a thermally activated CVD process for forming titanium nitride films on silicon substrates. The purpose of this invention is to lower the Cl-content in

15 the film and hence reduce its resistivity. This process includes two steps: In the first step a TiN film is deposited on the silicon substrate by passing both  $TiCl_4$  and  $NH_3$  gas into the reaction chamber. The second step is a subsequent post-annealing step in which  $NH_3$  gas only is passed into the

20 reaction chamber in order to remove residual chlorine atoms retained by the deposited TiN film.

For tribological applications thermally activated CVD deposition of hard ceramic coatings such as TiN, TiC and  $Al_2O_3$  on

25 hard metal (most often WC/Co composites) and HSS (High Speed Steel) is well-known in the art. However, thermally activated CVD is vitiated by the drawback that the substrate normally is heated to a temperature above  $850^\circ C$ . This may result in embrittlement of the hard metal substrates and

30 softens the steel substrate. Especially the softening of steel substrates is a problem, as hardened steels have to be rehardened after coating.

According to the present invention, a hard ceramic coating is deposited on the above-mentioned substrates since plasma activation allows the use of a lower deposition

temperature. However, it has been found that the adherence of films deposited by PA-CVD techniques is often too low for high performance applications.

5 Thus, it is an object of the present invention to provide a simple PA-CVD process for deposition of a solid metal-containing film onto the surface of a substrate containing at least 50% of Fe or WC by which the metallic component of the metal-containing film is introduced into the system as a  
10 metal halide and in which process the adhesion of the deposited film to the substrate is improved in comparison with films produced by prior art PA-CVD techniques involving introduction of metal halides.

15 According to the invention this object is accomplished by a PA-CVD process which is characterized in that it comprises the following steps a) to c):

a) feeding a first process gas essentially composed of:  
20 a metal halide, or  
a metal halide in combination with a diluent gas, a reduction agent, a non-metal precursor or any mixture thereof;

b) feeding a second process gas essentially composed of:  
25 a metal halide, a diluent gas, a reduction agent, a non-metal precursor or any mixture thereof,  
the mole fraction of metal halide in this second process gas being substantially lower than the mole fraction of metal halide in the process gas used in step a);

30 c) repeating steps a) and b) until a metal-containing film of the desired thickness has been formed.

metal-containing film covers pure metal films, pure Ce-

ramic films and metal films containing any amount of non-metal elements, including metal films in which a concentration gradient of non-metal elements is present such as in a nitrided layer. The term "ceramic" refers to materials comprising both metallic and non-metallic elements. The term "non-metal precursor" is defined as a gaseous starting compound providing the non-metallic element required for the formation of a ceramic film or a metal film containing non-metal elements during a CVD process. When e.g. TiC is formed from  $\text{TiCl}_4$  and  $\text{CH}_4$ , the latter compound is regarded as a non-metal precursor according to the above definition.

It is surprising that the presence of halogen-contaminants in films, in particular at the film/substrate interface, deposited from metal halides is responsible for the inferior adherence of such films. Moreover it is unforeseen that the concentration of halogen contaminants in the resulting film and/or film/substrate interface can be reduced (and hence the adherence improved) in a simple and efficient manner without adversely affecting the properties of the film by varying the content of metal halide in the process gas in intervals during the CVD process.

In other words, the present invention is based on the recognition that an improved adherence of the deposited film to the substrate can be achieved by shifting the process gas composition between a high and a low metal halide level.

The content of metal halide in the second process gas is substantially lower than the content of metal halide in the first process gas. More specifically the content of metal halide in the second process gas should be so low that the amount of unwanted halogen in the resulting film is reduced

The mole fraction of metal halide in the process gas used in step b) is preferably 0 to 0.5 times, more preferably 0 to 0.1 times, the mole fraction of metal halide in the process gas used in step a).

5

In a particular preferred embodiment of the invention the process gas used in step b) contains essentially no metal halide.

- 10 The time intervals and gas compositions used in step a) as well as step b) may differ from time to time during the repetition of these steps.

- 15 The first process gas used in step a) is preferably fed for 1 to 1000 seconds, more preferably for 25 to 250 seconds.

- 20 The second process gas used in step b) should be fed for a time interval sufficiently long for a reduction of the halogen-content of the deposit formed in step a) to a desired level to occur. It is preferably fed for 1 to 5000 seconds, more preferably for 10 to 3600 seconds, and even more preferably for 60 to 1800 seconds

- 25 When the process of the invention is used for deposition of a pure metal film onto a substrate, the process gases used in the above-mentioned steps a) and b) essentially contain no non-metal precursors. When, on the other hand, the process of the invention is used for deposition of a ceramic film, a non-metal precursor should always be present either  
30 in the process gas of step a) or in the process gas of step b) or in both.

The choice of metal halide naturally depends on the desired

metal such as Ti, Cr, W, Mo, V, Hf and Ta, are preferred.



The metal halide furthermore contains halogen atoms such as F, Cl and Br, preferably Cl. The process gas can contain two or more metal halides simultaneously. In this way it is possible to deposit e.g. metal alloy films and ceramic films comprising two or more metallic components.

The choice of non-metal precursor in case of deposition of ceramic films or metal films containing non-metal elements depends on the desired chemical constitution of the film. N<sub>2</sub> and NH<sub>3</sub> are examples of suitable non-metal precursors for the deposition of nitrogen-containing ceramic or metal films. CH<sub>4</sub> is an example of a suitable non-metal precursor for the deposition of carbon-containing ceramic or metal films. The process gas can contain two or more different non-metal precursors. Process gases containing two or more non-metal precursors can e.g. be used for deposition of ceramic films comprising two or more non-metallic components.

Suitable reduction agents are those capable of reducing the metal halide of the process gas. H<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub> and CH<sub>3</sub>CN are the preferred reduction agents.

The diluent gas is preferably a noble gas such as argon or helium.

The above-mentioned steps a) and b) are repeated until a film of the desired thickness is formed on the substrate. The said steps are preferably repeated at least once, more preferably 1 to 100 times, even more preferably 1 to 5 times. The thickness of the film may be varied between very wide limits depending a.o. on the desired properties of the film (including tribological properties) which of course depend on the end use of the product. The preferred thickness

The film thickness can be measured on a cross-section of the substrate either by optical microscopical methods or by electron microscopical methods. Numerous alternative methods are however available, and may be utilized as well.

5

In an embodiment of the invention there is provided a PA-CVD process for depositing a ceramic film or a metal film containing non-metal elements onto the surface of a substrate containing at least 50% Fe or WC, the process being characterized in that it comprises the steps of

10

a) feeding a first process gas essentially composed of:  
a metal halide, or  
a metal halide in combination with a diluent gas, a reduction agent or any mixture thereof;

15

b) feeding a second process gas essentially composed of:  
a metal halide, a diluent gas, a reduction agent or any mixture thereof,  
the mole fraction of metal halide in this process gas being substantially lower than the mole fraction of metal halide in the process gas used in step a);

20

c) repeating steps a) and b) until a metal film of a desired thickness has been formed;

25

d) feeding a third process gas essentially composed of:  
a non-metal precursor, or  
a non-metal precursor in combination with a reduction agent,  
a diluent gas or any mixture thereof; and

30

e) repeating steps a) to d) until a metal-containing film of a desired thickness has been formed.

For the purpose of the present invention, a low level of halogen contamination is deposited on the sub-

strate. In step d) this metal layer is reacted with a non-metal precursor resulting in the formation of a layer of ceramic or a layer of metal containing non-metal elements (e.g. a nitrided layer). Then steps a) to d) are repeated  
5 until a ceramic film or a metal film containing non-metal elements of the desired thickness has been formed.

The third process gas used in step d) should be fed for a time interval sufficiently long for a reaction to a desired  
10 extent (e.g. a desired concentration gradient) between the metal film formed during steps a) to c) and the non-metal precursor to occur. The time intervals actually used depend also of the thickness of the metal film formed during steps a) to c). The third process gas is preferably fed for a time  
15 interval of 0.01 to 100, more preferably 0.1 to 10 times, the total time used during steps a) to c).

In a particular embodiment of the invention the metal film formed as a result of steps a) to c) is completely transformed into a ceramic film in step d). In this case the metal  
20 film should be so thin that the entire metal film can be reacted with the non-metal precursor in step d). The preferred thickness of the metal film for complete transformation is 10 to 2000 nm.

25 The PA-CVD process of the invention (also referred to as "the pulsed PA-CVD process") is optionally followed by an ordinary continuous PA-CVD process. This may in particular be advantageous when the problem of insufficient adherence  
30 is caused primarily by the presence of halogen contaminants at the film/substrate interface. This process is preferably carried out by using a continuously fed process gas composed of:

0 to 30 % of a non-metal precursor,

1 to 98 % of a reduction agent,  
the balance being a diluent gas.

5 An equipment normally used for thermal activated CVD consists in general of three main parts: a gas supply system, a heated vessel and a vacuum pump.

10 From the gas supply system, operated at near ambient pressure, the gas mixture is lead into the heated vessel, which is pumped to the desired pressure utilized for the CVD reactions. From the pump the waste gasses can be bubbled through a scrubber to neutralize hazardous waste products formed during operation of the equipment.

15 Since pure thermal activation is not sufficient to promote the chemical reactions involved in the process according to the invention, additional energy is transferred to the gas by plasma excitation.

20 The process gas is preferably activated by combining heating of the vessel (thermal activation) and excitation of the gas by electric fields (plasma activation). Thus, the process according to the invention is of the type normally referred to as plasma assisted chemical vapour deposition (PA-CVD).

25 The applied electric field may be either of the DC, low frequency AC or RF type. When the deposited film is a poor electrical conductor, an RF electric field is preferred.

30 In order to obtain a proper plasma excitation of the gas, the gas pressure is suitably selected according to the following principles: If the gas pressure is too low, the plasma will extinguish. If on the other hand the gas pressure is too high, sparks may form between the electrodes.

The vessel temperature is suitably between ambient temperature and 1500°C.

5 In the following examples deposition of metal-containing films using the process of the invention is illustrated.

10 The vessel used in all examples is a cylinder having a diameter of approximately 150 mm and a height of 500 mm. Only the upper 350 mm of the vessel is heated. The gasses are introduced into the vessel through a distributor made from a steel tube with numerous small holes, all located near the top of the reactor vessel. The vessel is pumped through a hole in the bottom. The specimens are placed on a holder located 300 mm from the bottom of the vessel.

15 The chlorine content of the formed films is measured by Energy Dispersive X-ray analysis (EDX) or Secondary Ion Mass Spectroscopy (SIMS).

20 The adherence of the formed films to the substrate is measured using the test method developed by Daimler-Benz AG (VDI-richtlinie 3198, HRC adhesive test).

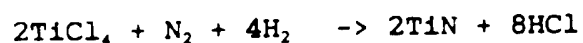
25 Unless otherwise stated, all percentages given in the following examples are percentages by mole.

#### EXAMPLE I

PA-CVD deposition of a titanium nitride film on a steel substrate using DC plasma excitation.

30

General reaction scheme:



Ar was fed into the vessel. A DC voltage of 550V was applied

in order to create a H<sub>2</sub>/Ar plasma. The H<sub>2</sub>/Ar plasma was maintained for 60 minutes in order to clean the substrate surface.

- 5 Following the preliminary plasma cleaning, the gas composition was varied by repeating the following gas composition sequence four times:

Feed time (s)	H <sub>2</sub> (%)	N <sub>2</sub> (%)	Ar (%)	TiCl <sub>4</sub> (%)
60	50	0	48	2
240	50	0	50	0

- 10 This gas composition sequence resulted in the formation of a Ti rich layer at the substrate surface.

Then a gas having the following composition was fed into the vessel for a period of 1200 seconds:

15

H <sub>2</sub> (%)	N <sub>2</sub> (%)	Ar (%)	TiCl <sub>4</sub> (%)
40	20	40	0

This resulted in the formation of a TiN nitriding layer on the substrate surface.

- 20 Following the above steps, continuous deposition of TiN was carried out using a conventional constant gas flow scheme and a process gas having the following composition:

H <sub>2</sub> (%)	N <sub>2</sub> (%)	Ar (%)	TiCl <sub>4</sub> (%)
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The continuous deposition was carried out for 60 minutes.

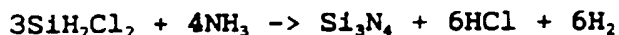
The total gas pressure in the vessel was kept at approximately 1 mbar and the vessel temperature was kept at 500 °C during the entire operation.

A TiN film having a thickness of 1 µm and containing essentially no Cl contaminants in the interface between the substrate and the TiN film was produced according to this example.

#### EXAMPLE II

PA-CVD deposition of a silicon nitride film on a steel substrate using RF plasma excitation

General reaction scheme:



The substrate was placed on a holder in the vessel. The vessel was heated to 750 °C and a gas composed of 70% H<sub>2</sub> and 30% Ar was fed into the vessel. An RF electric field (frequency: 13.56 MHz, power: 50 W) was applied in order to create a H<sub>2</sub>/Ar plasma. The H<sub>2</sub>/Ar plasma was maintained for 60 minutes in order to clean the substrate surface.

Following the preliminary plasma cleaning, the gas composition was varied by constantly repeating the following gas composition sequence 50 times:

Feed time (s)	NH <sub>3</sub> (%)	Ar (%)	SiH <sub>2</sub> Cl <sub>2</sub> (%)	H <sub>2</sub> (%)
50	90	0	10	0

The total gas pressure in the vessel was kept at approximately 0.5 mbar and the vessel temperature was kept at 750 °C during the entire operation.

- 5 The above gas composition sequence resulted in the formation of a 1  $\mu\text{m}$  thick  $\text{Si}_3\text{N}_4$  film at the substrate surface containing less than 0.3% Cl contaminants.

#### COMPARATIVE EXAMPLE I

- 10 PA-CVD deposition of a silicon nitride film on a steel substrate using RF plasma excitation and a constant gas composition

- 15 This Example was carried out as described in Example II with the exception that a process gas having the following composition was continuously fed into the vessel:

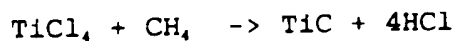
$\text{NH}_3$ (%)	$\text{SiH}_2\text{Cl}_2$ (%)
90	10

- 20 After a period of 60 minutes a 1  $\mu\text{m}$  thick  $\text{Si}_3\text{N}_4$  film was deposited on the substrate surface. According to analysis 0.4% Cl was trapped in the film as a contaminant.

#### EXAMPLE III

- 25 Deposition of a titanium carbide film on a steel substrate using RF plasma excitation.

General reaction scheme:



Steel was heated to 750 °C and gas composition



Ar was fed into the vessel. A RF electric field (frequency: 13.56 MHz, power: 100 W) was applied in order to create a H<sub>2</sub>/Ar plasma. The H<sub>2</sub>/Ar plasma was maintained for 60 minutes in order to clean the substrate surface.

5

Following the preliminary plasma cleaning, the gas composition was varied by constantly repeating the following gas composition sequence for a period of 60 minutes:

Feed time (s)	H <sub>2</sub> (%)	CH <sub>4</sub> (%)	Ar (%)	TiCl <sub>4</sub> (%)
100	75	5	13.5	1.5
100	50	0	50	0

10

The total gas pressure in the vessel was kept at approximately 0.4 mbar and the vessel temperature was kept at 750 °C during the entire operation.

15 The above gas composition sequence resulted in the formation of a TiC film showing good adherence to the substrate.

#### COMPARATIVE EXAMPLE II

20 PA-CVD deposition of a titanium carbide film on a steel substrate using RF plasma excitation and a constant gas composition

This Example was carried out as described in Example III with the exception that a process gas having the following composition was continuously fed into the vessel:

H <sub>2</sub> (%)	CH <sub>4</sub> (%)	Ar (%)	TiCl <sub>4</sub> (%)
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After a period of 60 minutes a 1  $\mu\text{m}$  thick TiC film was deposited on the substrate surface. The film showed inferior adherence to the substrate due to chlorine contamination.

Claims.

1. A plasma assisted chemical vapour deposition (PA-CVD) process for deposition of a solid metal-containing film onto the surface of a substrate containing at least 50% of Fe or WC, by which the metallic component of the metal-containing film is introduced into the system as a metal halide, characterized in that it comprises the following steps a) to c):
- a) feeding a first process gas essentially composed of:  
a metal halide, or  
a metal halide in combination with a diluent gas, a reduction agent, a non-metal precursor or any mixture thereof;
- b) feeding a second process gas essentially composed of:  
a metal halide, a diluent gas, a reduction agent, a non-metal precursor or any mixture thereof,  
the mole fraction of metal halide in this second process gas being substantially lower than the mole fraction of metal halide in the first process gas used in step a);
- c) repeating step a) and b) until a metal-containing film of a desired thickness has been formed.
2. A process according to claim 1, characterized in that the mole fraction of metal halide in the process gas used in step b) is 0 to 0.5, preferably 0 to 0.1, times the mole fraction of metal halide in the process gas used in step a).
3. A process according to claim 1 or 2, characterized in that it comprises the following steps a) to
- a) feeding a first process gas essentially composed of.

a metal halide, or

a metal halide in combination with a diluent gas, a reduction agent or any mixture thereof;

- 5 b) feeding a second process gas essentially composed of:  
a metal halide, a diluent gas, a reduction agent or any mixture thereof,  
the mole fraction of metal halide in this second process gas  
being substantially lower than the mole fraction of metal  
10 halide in the first process gas used in step a);

c) repeating step a) and b) until a metal film of a desired thickness has been formed;

- 15 d) feeding a third process gas essentially composed of:  
a non-metal precursor, or  
a non-metal precursor in combination with a reduction agent,  
a diluent gas or any mixture thereof; and

- 20 e) repeating step a) to d) until a metal-containing film of a desired thickness has been formed.

4. A process according to claim 3, characterized in that the repeating of step a) and b) in step c) is  
25 carried out until a metal film having a thickness of 10 to 2000 nm has been formed.

5. A process according to any of the preceding claims, characterized in that the last step of the  
30 process is followed by chemical vapour deposition of a metal-containing film using a continuously fed process gas essentially composed of:

1 to 98 % of a reduction agent,

the balance being a diluent gas.

6. A process according to any of the preceding claims,  
c h a r a c t e r i z e d in that the metal halide contains  
5 a metal preferably selected among Al, Si or transition met-  
als, preferably Ti, Cr, W, Mo, V, Hf and Ta.

7. A process according to any of the preceding claims,  
c h a r a c t e r i z e d in that the reduction agent is a  
10 compound capable of reducing the metal halide, preferably  
selected among  $H_2$ ,  $CH_4$ ,  $NH_3$  and  $CH_3CN$ .

8. A process according to any of the preceding claims,  
c h a r a c t e r i z e d in that the non-metal precursor  
15 is  $N_2$ ,  $CH_4$ ,  $NH_3$  or  $CH_3CN$ .

9. A process according to any of the preceding claims,  
c h a r a c t e r i z e d in that the diluent gas is a no-  
ble gas, preferably argon.

20

10. A process according to any of the preceding claims,  
c h a r a c t e r i z e d in that the substrate essentially  
consists of hard metal, preferably a WC/Co composit, or  
steel, preferably HSS (High Speed Steel).

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 95/00505

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C23C 16/08, C23C 16/30, C23C 16/50

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WPI

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Dialog Information Services, File 351, World Patent Index 81-96, Dialog accession no. 007546088, WPI accession no. 88-180020/26, HITACHI LTD et al: "Glow discharge decomposition of halide to form coating on substrate using periodic introduction of halide during the process"; & JP,A,63118075,880523, 8826 (Basic) & Patent abstracts of Japan, Vol 12, Nr 365, C-532, abstract of JP, A, 63-118075 (HITACHI LTD), 23 May 1988 (23.05.88)	1,2,5-10
Y	--	3,4
Y	US 4749597 A (JOHN MENDONCA ET AL), 7 June 1988 (07.06.88), column 1, line 59 - line 68; column 2, line 55 - column 3, line 27; column 4, line 3 - line 10, claim 1, abstract	3,4
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☒ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other

document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, the combination being obvious to a person skilled in the art

document member of the same patent family

Date of the actual completion of the international search

11 April 1996

Name and mailing address of the ISA/  
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Date of mailing of the international search report

12 -04- 1996

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 95/00505

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SURFACE AND COATINGS TECHNOLOGY, Volume 54/55, 1992, Kazuki Kawata, "Development of mass-production-type plasma chemical vapour deposition equipment and its application to various dies", page 604 - page 608, see page 604 - page 606 and abstract --	6-10
A	EP 0032887 A1 (SANDVIK AKTIEBOLAG), 29 July 1981 (29.07.81), page 15, line 15 - line 24; page 25, line 15 - line 23, claim 1 --	6-8,10
A	US 3565676 A (R.A. HOLZL), 23 February 1971 (23.02.71), column 2, line 27 - line 36; column 9, line 8 - column 10, line 15, abstract --	1,6,7,9,10
A	US 5279857 A (ERIC C. EICHMAN ET AL), 18 January 1994 (18.01.94), column 1, line 58 - column 2, line 16; column 2, line 35 - line 48; column 3, line 3 - line 40, claims 1,4-6, abstract -- -----	1,2,6-9

INTERNATIONAL SEARCH REPORT  
Information on patent family members

05/02/96

International application No.  
PCT/DK 95/00505

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4749597	07/06/88	NONE	
EP-A1- 0032887	29/07/81	SE-T3- 0032887 JP-C- 1586721 JP-A- 56145181 US-A- 4399168 US-A- 4282289	19/11/90 11/11/81 16/08/83 04/08/81
US-A- 3565676	23/02/71	NONE	
US-A- 5279857	18/01/94	AU-A- 2485492 CA-A- 2114716 DE-D- 69206808 EP-A,B- 0599991 JP-T- 6510089 US-A- 5308655 WO-A- 9304214	16/03/93 04/03/93 00/00/00 08/06/94 10/11/94 03/05/94 04/03/93